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(54) PROCESS FOR THE PREPARATION OF NOVEL TECHNICALLY VALUABLE PRODUCTS FROM MINERAL OIL DISTILLATES OR FROM SOLVENT EXTRACTS OF SUCH DISTILLATES

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The present invention relates to a method for the preparation of products from mineral oil distillates or from solvent extracts of such distillates.

The present invention provides a process for the preparation of products, which may be technically valuable, from mineral oil distillates or from solvent extracts of such distillates, which process comprises oxidizing one or more mineral oil distillates and/or solvent extracts of mineral oil distillates having a content of aromatically bound carbon corresponding to a VGC-value of at least 0.85, preferably at least 0.90, and an average molecular weight of 150 to 600, preferably 200 to 500, by blowing oxygen, preferably in the form of air, thereinto and fractionating the oxidized distillate and/or extract, at least one product fraction having a boiling point interval in the temperature range of from about 320°C to about 420°C at 760 mm Hg and another product fraction having a lowest boiling temperature of 400°C or above at 760 mm Hg being isolated in the fractionation and products obtained by this process.

According to the present invention it has been found that, inter alia, a product fraction comprising a light oil which may possess extremely valuable properties as regards stability to oxidation and which can be used as a process oil can be obtained by oxidation of one or more mineral oil distillates and/or solvent extracts from mineral oil distillates having a certain minimum content of aromatically bound carbon by blowing air thereinto and subsequent distillation of the oxidized distillate and/or extract and collection of certain product fractions at temperatures up to about 375°C at 760 mm Hg. Another product

fraction proved to be valuable as an additive in moulding compounds for gramophone records by enabling increased product rate and improved sound reproduction. A possible third fraction lying between these two first fractions may be used as a process oil. This third fraction may have a boiling point interval of about 375 to 420°C at 760 mm Hg.

The different product fractions which may be obtained in accordance with the invention can thus extend over the whole temperature range of 320 to 420°C or over a narrower range within this range. If a lower flash point or a darker colour of the first product fraction is considered to be tolerable it is possible to allow the boiling temperature of a minor part of the fraction to lie a little below 320°C at 760 mm Hg, for instance down to about 315°C, and/or a little above 420°C at 760 mm Hg. Similarly, minor amounts of components boiling at temperatures a little below 400°C at 760 mm Hg can be allowed to be present in the second product fraction if the stickiness of the product caused thereby is considered to be tolerable.

According to a preferred embodiment of the process according to the invention the different product fractions are collected in separate steps each of which is preceded by an oxidation step. The second product fraction can, for instance, be recovered by subjecting the bottom fraction remaining after distilling of the first product fraction to oxidation by blowing air thereinto whereafter components having a boiling point lower than the boiling point range of the desired fraction are removed by distillation or stripping.

According to another preferred embodiment of the invention, part of the substances leaving the distillate and/or the extract

with the oxidation gases in an oxidation step may be condensed and fed back into the process.

According to a further preferred embodiment of the invention, the oxidation is carried out in the presence of a catalyst, which is soluble in the oxidized distillate and/or extract or is converted into compounds which are soluble in the oxidized distillate and/or extract by reaction with the distillate and/or extract. The product fraction having a lowest boiling temperature of 400°C or above will in this way be given a higher penetration at equal softening point, which in practice means a decrease in the shortness of this product.

According to the invention the catalyst may, for instance, be a metal organic salt, a metal oxide or a mixture thereof, the catalyst preferably being used in an amount corresponding to 0.01 to 2 % by weight of metal calculated on the distillate or extract to be oxidized. The product fraction having a lowest boiling temperature of 400°C or above may as a consequence thereof contain from about 0.01 to about 3 % by weight of metal, calculated on the weight of said fraction.

Any metal known to function as a catalyst by continuous variation of its valency between two oxidation states may be used. Examples of such metals are chromium, cobalt, nickel, iron, copper, and manganese. In addition, zinc has proved to function excellently as catalyst metal in accordance with the invention.

The metal organic salts may, for instance, be naphthenates or salts of aliphatic carboxylic acids. The organic part of the salt is preferably as small as possible. Naphthenates, acetates, propionates and butyrates are especially preferred salts.

Irrespectively of whether the catalyst is added in the form of an oxide or a metal organic compound the metal will be present in the same final form in the residue after the distillation.

The oxidation is carried out in the presence as well as in the absence of a catalyst for a period of at least 7 hours in order to obtain a softening point of the residue after distillation of at least 100°C, preferably within the range of from 105 to 140°C. Products having a softening point above 140°C cannot easily be brought in a particulate form by spray cooling but will have to be brought into said form by grinding.

The product fraction boiling at 375 to 400°C can be collected in a separate distillation step, but may also be collected from the same distillation column as either of the two other fractions. In principle it is of course possible to collect all three product fractions from one and the same column but, as mentioned above, the product fractions are preferably collected in separate steps, each of which is preceded by an oxidation step.

Each oxidation step may, if desired, be divided into several sub-steps. Such a division may especially be contemplated for the strong first oxidation step.

The oxidation is suitably carried out at a temperature of from 180° to 300°C at 760 mm Hg.

The hot second product fraction coming from the process may be spray cooled to yield a preferred form of product which may be handled particularly easily.

Any fraction obtained by distillation of a mineral oil and having a content of aromatically bound carbon corresponding to a VGC-value of at least 0.85, preferably at least 0.90, and an average molecular weight of 150 to 600, preferably 200 to 500, may be used as a mineral oil distillate to serve as the starting material in the process according to the invention. Lubricating oil distillates having a boiling point interval of 250 to 295°C, 295 to 340°C, 340 to 385°C, 385 to 440°C or 440 to 490°C, corresponding to an average molecular weight of about 210, 250, 295, 350, and 425, respectively, are examples of such fractions.

The term "solvent extracts of mineral oil distillates" is used herein to designate products obtained in any suitable way by extraction of mineral oil distillates with, for example, furfural, cresol, phenol, or liquid SO_2. In order to be suitable for use in the process of the invention the extracts should have a content of aromatically bound carbon and an average molecular weight in accordance with what has been stated for the mineral oil distillates above.

The VGC-value (VGC = Viscosity Gravity Constant) is a standard measure for the aromatic contents of mineral oil products and is determined according to ASTM D 2140. A VGC-value of 0.85 generally corresponds to a content of aromatically bound carbon of about 10 to 30 %, while a VGC-value of 0.90 generally corresponds to an aromatic carbon content of about 25 to 40 %, calculated on the total amount of carbon.

The proportions obtained of the different fractions can be adjusted by proper choice of the oxidation time and of the average molecular weight of the starting material. A longer

oxidation time or an increased average molecular weight gives higher yields of the second product fraction.

The following Examples illustrate the invention:

Example 1

3.0 l of an extract obtained from a lubricating oil distillate in the boiling point interval 295 to 340°C and having a VGC-value of 0.958 were oxidized by blowing air into the extract (3 l/min) with total reflux and separation of water formed, the oxidation taking place firstly for 5 hours at 240°C and then for 4 hours at 300°C. The viscosity at 98.9°C (210°F) thereby increased from 2 cSt to 80 cSt. Distillation was then carried out in vacuo (about 0.3 mm Hg). A top fraction having a boiling point at 760 mm Hg of up to 325°C was collected, the yield being 10 %. Then a medium fraction in the range of 325 to 375°C at 760 mm Hg was collected, the yield being 30 %. Another fraction was collected at 375 to 400°C at 760 mm Hg, the yield being 10 %. A product boiling above 400°C at 760 mmHg and having a softening point (Ringand Ball) of 116°C was obtained as the residue, yield 50 %. (All yields are calculated on the weight before the distillation.)

Example 2

Example 1 was repeated, starting, however, from an extract of a lubricating oil in the boiling point range 440 to 490°C. The VGC-value of the extract was 0.961. Air was blown into the extract for 3 hours at 240°C with no feedback of condensate and for 4 hours at 300°C with feed-back of condensate. The yield of top fraction was about 3 %, that of product in the interval 325 to 375°C about 8 %, in the interval 375 to 400°C about 5 % and of bottom fraction 84 %, all yields being calculated on the weight before the distillation.

Example 3

3.0 l of an extract obtained from a lubricating oil in the boiling point range 340 to 385°C and having a VGC-value of 0.960 were oxidized by blowing air into the extract (3 l/min), with total reflux and separation of the water formed, for 10 hours at 300°C. The softening point of the material was then 88°C (Ring and Ball).

Distillation was then carried out in vacuo (about 0.3 mm Hg). A top fraction having a boiling point at 760 mm Hg of up to 375°C was collected, the yield being 4 % by weight. Then a fraction in the range 375 to 400°C at 760 mm Hg was collected, the yield being 18 % by weight. A product boiling above 400°C at 760 mm Hg and having a softening point (Ring and Ball) of 124°C was obtained as the residue, the yield being 71 % calculated on the weight before the oxidation.

Example 4

3.0 l of an extract obtained from a lubricating oil in the boiling point range of 340 to 385°C and having a VGC-value of 0.960 were oxidized by blowing air into the extract (3 l/min) in the presence of 0.5 % by weight of ZnO (0.44 % by weight of Zn, calculated on the weight of the extract), with total reflux and separation of the water formed, for 11 hours at 300°C. The softening point of the material was then 83°C (Ring and Ball).

Distillation was then carried out in vacuo (about 0.3 mm Hg). A fraction having a boiling point at 760 mm Hg in the interval 320 to 375°C was collected, the yield being 4 %. Another fraction was collected at 375 to 400°C at 760 mm Hg, the yield being 16 %. A homogeneous product boiling above 400°C at 760 mm Hg and having a softening point (Ring and Ball)

of 123°C was obtained as the residue, yield 80 %, calculated on the weight of the extract before the oxidation. The penetration (according to IP 49) was measured to be 3 mm/10 at a load of 100 g for 5 seconds and for 500 seconds. The penetration for a corresponding product fraction obtained without using a catalyst was 0 mm/10 respectively 6 mm/10 at a load of 100 g for 5 respectively 500 seconds.

Example 5

An extract according to Example 4 was oxidized in the same way as described in Example 4 but the zinc oxide was replaced by 2 % by weight of cobalt naphthenate (0.25 % by weight of Co, calculated on the weight of the extract) as the catalyst and oxidation was carried out for 10 hours. The softening point of the material was then 83°C (Ring and Ball).

Distillation was then carried out in vacuo (about 0.3 mm Hg). A fraction having a boiling point at 760 mm Hg in the interval 320 - 400°C was collected, the yield being 19 %. A homogeneous product boiling above 400°C at 760 mm Hg and having a softening point (Ring and Ball) of 109°C was obtained as the residue, yield 81 %, calculated on the weight of the extract before the oxidation. The penetration (according to IP 49) was 2.5 and 3 mm/10 at 5 and 500 seconds, respectively, load 100 g.

Example 6

An extract according to Example 4 was oxidized in the same way as described in Example 4 but the zinc oxide was replaced by 1 % by weight of copper acetate (0.32 % by weight of Cu, calculated on the weight of the extract) as the catalyst

and oxidation was carried out for 12 hours. The softening point of the material was then 80°C.

Distillation was then carried out in vacuo (about 0.3 mm Hg). A first fraction having a boiling point at 760 mm Hg in the interval 320 to 360°C and a second fraction having a boiling point at 760 mm Hg in the interval 360 to 400°C were collected, the yields being 2 and 18 %, respectively. A homogeneous product boiling above 400°C at 760 mm Hg and having a softening point (Ring and Ball) of 108°C was obtained, as the residue, yield 80 %, calculated on the weight of the extract before the oxidation. The penetration (according to IP 49) was 2 mm/10 at 5 as well as at 500 seconds, load 100 g.

Example 7

3.0 l of an extract obtained from a lubricating oil distillate in the boiling point interval 340 to 385°C and having a VGC-value of 0.95 were oxidized by blowing air into the extract (3 l/min) in the presence of 0.5 % by weight of ZnO (0.44 % by weight of Zn calculated on the weight of the extract) with total reflux and separation of water formed, for 12 hours at 270°C. The softening point of the material was then 89°C (Ring and Ball).

Distillation was then carried out in vacuo (about 0.3 mm Hg). A fraction having a boiling point at 760 mm Hg in the range 320 to 400°C was collected, the yield being 19.5 %. A homogeneous product boiling above 400°C at 760 mm Hg and having a softening point (Ring and Ball) of 125°C was obtained as the residue, the yield being 80.5 %, calculated on the weight of the extract before the oxidation.

Example 8

3.0 l of an extract obtained from a lubricating oil distillate in the boiling point interval 295 - 340°C and having a VGC-value of 0.958 were oxidized by blowing air into the extract (3 l/min) with total reflux and separation of water formed, for 10 hours at 300°C. The softening point of the material was then 85°C (Ring and Ball).

1 part by weight of the oxidized extract thus obtained was after grinding mixed with 9 parts by weight of industrial benzine (boiling point 80 - 120°C) in a vessel while stirring at room temperature for 30 minutes. The supernatant was decanted off and the residue was washed with benzine, filtered and evaporated at 130°C. A homogeneous product having a softening point (Ring and Ball) >150°C and a lowest boiling point >420°C was obtained as the residue, the yield being about 50 % calculated on the weight of the extract before the oxidation.

The benzine was stripped off from the supernatant, whereafter distillation was carried out in vacuo (about 0.3 mm Hg), a fraction having a boiling point at 760 mm Hg in the range 320 to 420°C being collected.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of a product from a mineral oil distillate, which process comprises oxidizing a mineral oil distillate and/or a solvent extract of a mineral oil distillate by passing oxygen into the distillate or extract, the distillate or extract having an average molecular weight of from 150 to 600 and a content of aromatically bound carbon corresponding to a VGC-value of at least 0.85, fractionating the oxidized distillate and/or extract, and collecting at least one fraction having a boiling point interval within the temperature range of from about 320°C to 420°C at 760 mm Hg.

2. A process as claimed in Claim 1, wherein a fraction boiling at about 320°C to about 375°C at 760 mm Hg is collected.

3. A process as claimed in Claim 1, wherein the average molecular weight of the distillate or extract is from 200 to 500.

4. A process as claimed in Claim 1, wherein the content of aromatically bound carbon in the distillate or extract corresponds to a VGC-value of at least 0.90.

5. A process as claimed in Claim 1, wherein the oxygen is in the form of air.

6. A process as claimed in Claim 1, wherein a further fraction having a lowest boiling temperature of 400°C or above at 760 mm Hg is isolated.

7. A process as claimed in Claim 2, wherein the distillation residue obtained after distilling off the fraction boiling at about 320°C to about 375°C at 760 mm Hg is oxidized by passing oxygen into it, and a second fraction having a lowest boiling temperature of 400°C or above is isolated by distillation or by stripping off components with lower boiling points.

8. A process as claimed in Claim 6 or 7, wherein the hot fraction with the lowest boiling temperature of 400°C or above is spray cooled.

9. A process as claimed in Claim 2, wherein a further fraction having a boiling point in the range of from about 375°C to about 400°C at 760 mm Hg is also collected.

10. A process as claimed in Claim 9, wherein the further fraction is collected by distillation.

11. A process as claimed in Claim 6, 7 or 9, wherein the various fractions are collected in separate distillation steps, each of which steps is preceded by an oxidation step.

12. A process as claimed in Claim 1, wherein at least part of the substances escaping from the distillate and/or extract with the oxidation gases in an oxidation step is condensed and returned to the process.

13. A process as claimed in Claim 1, wherein the oxidation is carried out in the presence of a catalyst, which is soluble in the oxidized distillate and/or extract or is converted into compounds which are soluble in the oxidized distillate and/or extract by reaction with the distillate and/or extract.

14. A process as claimed in Claim 13, wherein the catalyst is a metal organic salt, a metal oxide or a mixture thereof.

15. A process as claimed in Claim 14, wherein the metal is chromium, cobalt, nickel, iron, copper, manganese, or zinc.

16. A process as claimed in Claim 14, wherein the metal organic salts are metal salts of naphthenic acids or of aliphatic carboxylic acids.

17. A process as claimed in Claim 16, wherein the carboxylic acid is acetic acid, propionic acid or butyric acid.

18. A process as claimed in Claim 13, wherein the amount of catalyst used corresponds to 0.01 to 2% by weight of

metal calculated on the distillate and/or extract to be oxidized.

19. A process as claimed in Claim 1, wherein the oxidation is carried out for at least 7 hours.

20. A process as claimed in Claim 6, wherein oxidation is carried out to a softening point Ring and Ball of at least 100°C of the fraction having a lowest boiling temperature of 400°C or above at 760 mm Hg.

21. A process as claimed in Claim 20, wherein the softening point is within the range of from 105 to 140°C.

22. A product having a lowest boiling point of 400°C or above at 760 mm Hg and a softening point of 100°C or above, said product being derived from mineral oil distillates and/or solvent extracts of mineral oil distillates having a content of aromatically bound carbon corresponding to a VGC-value of at least 0.85 and an average molecular weight of 150 to 600 by blowing oxygen thereinto and then fractionating off constituents having a boiling point lower than the lowest boiling point of the product.

23. A product according to Claim 22, which product contains 0.01 to 3% by weight of a metal in bound form.

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ABSTRACT OF THE DISCLOSURE

A process for the preparation of products, which may be technically valuable, from mineral oil distillates or from solvent extracts of such distillates is disclosed, which process comprises oxidizing one or more mineral oil distillates and/or solvent extracts of mineral oil distillates having a content of aromatically bound carbon corresponding to a VGC-value of at least 0.85, preferably at least 0.90, and an average molecular weight of 150 to 600, preferably 200 to 500, by blowing oxygen, preferably in the form of air, thereinto and fractionating the oxidized distillate and/or extract, at least one product fraction having a boiling point interval in the temperature range of from about 320°C to about 420°C at 760 mm Hg and another product fraction having a lowest boiling temperature of 400°C or above at 760 mm Hg being isolated in the fractionation and products obtained by this process.